

Int. Cl<sup>7</sup> : C05B 11/10 C05C 3/00 C05 G 3/06

194747

Ind. Cl : 123 I (4)

Title : A PROCESS FOR THE MANUFACTURE OF SLOW-RELEASE FERTILIZERS.

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Application no 10/CAL/1999 FILED ON 06.01.1999

*APPROPRIATE OFFICE FOR OPPOSITION PROCEEDING (RULE 4, PATENT RULES 2003) PATENT OFFICE KOLKATA.*

### 31CLAIMS.

A process for preparation of slow release cationic micronutraent fertilizers, which processes comprises heating at least one micronutrient metal or a compound thereof such as herein described with or without additives such as herein described with phosphoric acid till the resultant mixture is mostly homogenous, further heating to corresponding metal polyphosphates of such a degree of polymerisation that they are still soluble in dilute mineral acids and complexants, treating said metal polyphosphates with a basic compound and finally obtaining a dried powder

*Complete Specification : 33 pages.*

*Drawing : NIL*

**FORM-2**

**THE PATENTS ACT, 1970**

**( 39 of 1970 )**

**~~PROVISIONAL~~ / COMPLETE**

**SPECIFICATION**

**SECTION 10**

**TITLE**

A process for the manufacture of slow-release fertilizers

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The following specification particularly describes the nature of the  
invention and the manner in which it is to be performed

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06 JAN 1999  
06 APR 2000

ORIGINAL

### FIELD OF INVENTION

This invention relates to a process for the manufacture of slow-release fertilizers of cationic micronutrients such as zinc, copper, iron, manganese, cobalt or magnesium, either as single nutrient or as multinutrient formulations.

### BACKGROUND OF INVENTION

Compounds which are widely used today as micronutrient fertilizers, are soluble salts or organic chelated forms eg., zinc, copper, manganese or iron sulphates, and EDTA complexes of the same. Liquid fertilizers such as micronutrients dissolved in condensed phosphoric acid or ammonium polyphosphates are also used (V. Sauchelli, 1967, Chemistry and Technology of Fertilizers, Reinhold, New York; G.H. Collins, 1955, Commercial Fertilizers, McGraw Hill, New York). The synthesis of slow-release fertilizers based on phosphate glasses known as frits, have been described. Such frits are usually prepared by fusing ammonium or sodium dihydrogen

phosphates with micronutrient salts to produce a melt, at temperatures between 800 and 1400 C and then rapidly cooling the liquid by pouring on to a cold plate (G.J. Roberts, 1973, Am. Ceram. Soc. Bull., Vol 52, p. 383, <sup>of 1975</sup> ~~ibid. idem~~, Vol. 54, p 1069, Austrian Patent No. 326160/US Patent No. 3574591 of 1971, US Patent No. 2713536 of 1974.

Apart from phosphate glasses, other phosphate compounds have also been proposed as slow-release fertilizers. These include micronutrients added to metaphosphates of potassium or calcium prior to reaction. Volfkovich et al., (S.I. Volfkovich, A.S. Cherepanova, I.A. Grishina & G.A. Bitko, 1970, D. Zh. Nauki Kaz SSR (Russian) p. 3) added various metal oxides to potassium metaphosphate melts. Volfkovich reviewed the work done by the Russian school in the field of metaphosphate based fertilizers (S.I. Volfkovich, 1972, J. Appl. Chem (USSR), Vol. 45, p.2479). A Russian patent (Su <sup>of 1986</sup> 1270148) describes the production of such mixed metaphosphate based fertilizers produced at 550 -

of 1990  
880 C. Two Indian Patents (Nos. 172800/and 177205 of 1991) describe the processes for production of zinc and copper fertilizers based on low molecular weight polyphosphates. The chemistry of zinc and copper phosphate polymerisation and the chemical nature of these fertilizers have also been described (S.K. Ray, C. Varadachari & K. Ghosh, 1993, Ind. Eng. Chem. Res., Vol. 32, p. 1218; S.K. Ray, C. Varadachari & K. Ghosh, 1997, J. Agric. Food Chem., Vol., 45, p. 1447).

The major drawbacks of using soluble salts (such as sulphates), as micronutrients fertilizers are, leaching losses, chemical transformation losses, ground water contamination and low fertilizer-use efficiency. On the other hand, micronutrient fertilizers having slow-release properties do not suffer any of these disadvantages. However, both the existing types of slow-release fertilizers incorporating micronutrients, are not commercially successful so far.

The major disadvantage of the first group of compounds viz. the phosphate glass frits, is that

the process for their production is not commercially viable; the reaction conditions, in the melting of phosphates, are so corrosive that very expensive material have to be used for furnace construction thereby limiting large scale production and increasing product costs. The major disadvantage of the second group of compounds viz. the long chain metaphosphates is their excessive insolubility particularly in complexants, which renders the micronutrient ions mostly unavailable for plants. The most important factor here is that both these two types of phosphate based slow release fertilizers are essentially macronutrient (N, P or K) fertilizers containing micronutrients as supplements. There is no process available as yet for making a slow-release fertilizer that is essentially a source of micronutrients and which can thereby replace the conventional water-soluble micronutrient fertilizers.

OBJECTS OF THE INVENTION

An object of this invention is to propose a process for the manufacture of slow release fertilizers of cationic micronutrients having a substantial reduction in production time for the initial reaction stage between phosphoric acid and micronutrient compounds.

Another object of this invention is to propose a process for the manufacture of slow release fertilizers of cationic micronutrients and which has a simple method of assessing the upper limit of polymerisation whereby the process is rendered extremely flexible as regards choice of temperature for polymerisation and components in reacting mixture.

Yet another object of this invention is to propose a process for the manufacture of slow release fertilizers of cationic micronutrients and wherein a wide range of starting materials may be used in widely ranging proportions and the

polymerisation can be carried out at any convenient temperature.

Still another object of this invention is to propose a process for the manufacture of slow release fertilizers of cationic micronutrients which is simple, requires lower energy inputs than all previous processes and is readily adaptable to a wide range of micronutrient formulations.

#### DESCRIPTION OF THE INVENTION

According to this invention there is provided a process for the preparation of slow-release cationic micronutrient fertilizers, which comprises in heating at least one micronutrient metal or a compound thereof, with or without additives, with phosphoric acid till the resultant mixture is nearly homogeneous, further heating to form metal polyphosphates of such a degree of polymerisation that they are still soluble in dilute mineral acids and complexants, treating said metal polyphosphates with a basic compound and finally obtaining a dried powder.

Compound of the micronutrient element such as their oxides, hydroxides, carbonates, sulphates or chlorides are mixed with phosphoric acid and heated to a temperature  $T_1$  above  $150^\circ$  to remove excess water and allow completion of reaction. This reaction may also be carried out under vacuum, at temperature lower than  $150^\circ$ . The dihydrogen phosphates are then



further heated to a temperature  $T_2$  which is above temperature  $T_1$  till polyphosphates of the desired degree of polymerisation are produced as observed by their solubility characteristics or average chain length estimates. The polyphosphates are subsequently neutralised with bases like ammonia, lime, sodium or potassium hydroxide. The product is dried at low temperature powdered and sieved.

(i) Zinc Fertilizers

Starting materials include zinc oxide (containing upto 79% Zn), zinc metal (containing upto 99.99% Zn), zinc ash (containing zinc oxide and metallic zinc in variable amounts), zinc sulphate (containing up to 40.5% Zn) or zinc chloride (containing upto 47.9% Zn). The zinc raw material is added to phosphoric acid (containing not more than 60%  $P_2O_5$ ) so that the molar ratio of Zn:P in the mixture is at least 1:2 (weight ratio Zn:P is at least 1.05:1). The optimum molar ratio of Zn:P is 1:2. With P levels higher than this the initial reaction is faster but at the same time more acid groups will remain in the polyphosphate and this will require more base for neutralisation. Almost any grade of acid can be used for the reaction. However, fertilizer grade phosphoric acids containing about 30-60%  $P_2O_5$  are suitable and since acid containing about 50%  $P_2O_5$  is the most commonly available this is preferred for the

reaction. The mixture of zinc compounds and phosphoric acid is taken in a porcelain crucible or a tray made of SS 316L, placed in a muffle furnace and heated at any temperature above 150°C. At higher temperatures evaporation is faster. The optimum temperature is determined by the nature of the equipment used for evaporation. Thus, in a muffle furnace 170°C is optimum; in commercial driers like a spray drier input temperatures of about 400°C may be needed but the duration of heating is very small and product temperatures do not exceed 200°C. When evaporation is done under partial vacuum reaction temperatures may be reduced. After the reaction, the product contains mostly zinc dihydrogen phosphate; some sulphate or chloride may also be present if such raw materials have been used. This product is further heated at any temperature above 150°C for polyphosphates to form. Here again, the temperature used for polymerisation depends on the equipment used for the reaction. In a muffle furnace 350°C is optimum. If a fluidised bed furnace is used 400°C is preferred. Heating is done till a polyphosphate of the desired degree of polymerisation is obtained. When such reaction is carried out in trays or similar vessels about 60 min is required at 350°C furnace temperatures. When the reaction is done in a fluidised bed furnace only about 15 min is required at 400°C furnace temperatures. the product is tested at periodic intervals for

solubility in 0.1 N HCl, 0.33 M citric acid, 0.005 M DTPA. Polymerisation may be stopped at any stage wherein the product retains its solubility in the aforesaid reagents; the product will be observed mostly to dissolve in these reagents within 30 min. The optimum polymerisation stage is that prior to the formation of a product which is significantly insoluble in the acids and complexants mentioned above; in other words, the product has reached the upper limit of its solubility in these reagents. Subsequently, the reaction product is cooled to room temperature, made into a slurry with water and mixed with ammonia solution, CaO (lime), CaCO<sub>3</sub> (limestone), sodium carbonate (soda ash), potassium carbonate, sodium hydroxide or potassium hydroxide. Enough bases are added to raise the pH of the slurry to between 3 and 4. Too little base will result in a hygroscopic product. Too much of base has no particular advantage and may precipitate of some of the zinc ions. After neutralising, when the pH has stabilised, the material is dried at <100°C, preferably at 60-80°C. It is then ground and sieved, preferably to <100 mesh B.S.

(ii) Copper fertilizers

Starting materials include the hydroxide carbonate, sulphate or chloride of the cupric ion containing up to 49.9%, 51.4%, 25.4% and 47.0% Cu respectively. The copper raw material

is added to phosphoric acid (containing up to 60% of  $P_2O_5$ ) so that the molar ratio of Cu:P is 1:2 or higher (weight ratio of Cu:P is at least 1.02:1). The optimum molar ratio of Cu:P is 1:3. With P ratios lower than this the cupric polyphosphate tends to insolubilise so rapidly that reaction control may be difficult. This problem is overcome at the Cu:P = 1.3 ratio. Higher ratios of P may also be used but are of no particular advantage. All other stages of manufacture are as described above for the zinc fertilizer. Polymerisation temperature and period of heating are equipment dependant, generally lower temperatures are required than for the zinc compounds. When the reaction is carried out in a muffle furnace 250 - 300 C is optimum. Polymerisation is stopped before insolubilisation in the acids and complexants occurs.

(iii) Iron fertilizers

Starting materials include oxides (eg. hematite), oxyhydroxides (eg. goethite), sulphate or chloride form of ferric iron, iron metal (eg. iron filings), ferrous sulphate or ferrous chloride containing up to 69.9%, 62.8%, 27.9%, 34.4%, 99.9%, 36.7% or 44.9% Fe respectively. The iron raw material is added to phosphoric acid (containing up to 60%  $P_2O_5$ ) so that the molar ratio of Fe:P is at least 1:3 (weight ratio 1:1.67) where ferric compounds are used and at least 1:2 (weight ratio 1:1.11) where iron metal or ferrous compounds are used. The optimum molar ratio of Fe:P in the case of ferric compounds is 1:3 and in case

of ferrous compounds it is 1:2. All other reaction parameters are broadly as described for the zinc fertilizers. Polymerisation, however, occurs at a lower temperature than with the zinc phosphates and the polyphosphate formed is also more insoluble in dilute acids and complexants. Iron fertilizers prepared with additives have improved properties; magnesium oxide is best suited for this purpose. The optimum molar ratio of Fe:Mg is 1:3. When MgO additive is used, the amount of phosphoric acid is also increased. Thus, for every mole of Mg, at least 2 moles of phosphoric acid are to be added (Mg:P=1:2). The mixture of iron salt, magnesium oxide and phosphoric acid is heated at above 150 C as described for the zinc fertilizer. Reaction is continued at least till a viscous gel is obtained and little unreacted material remains. This material is subsequently polymerised, by heating at any temperature above 200 C, whereupon iron magnesium polyphosphate is obtained. reaction is optimum at 250 C, whereupon iron magnesium polyphosphate is obtained reaction is optimum at 250 C. However, depending on the nature of reaction and heat contact period, reactions may also be carried out at higher temperatures. The polyphosphate with maximum solubility in the testing reagents (0.1 N HCl, 0.33 M citric acid, 0.005 M DTPA) is chosen. It is subsequently neutralised with ammonia solution or with magnesium oxide in the presence of sufficient water to allow the neutralisation reaction to occur. Any basic

compound may be used but magnesium oxide gives the best results; the final pH of the slurry should be between 4.5 and 6; the optimum pH is 5.4. The neutralised material is then dried, at temperatures lower than 100°C (preferably at 60-80°C), finally, it is ground to a powder which passes through a 100 mesh BS sieve.

(iv) Manganese fertilizers

Starting materials include manganese dioxide or manganous oxide or sulphate which may contain up to 63.1%, 77.4% or 36.4% Mn respectively. The manganese raw material is added to phosphoric acid such that the molar ratio of Mn:P is at least 1:4 (weight ratio Mn:P 1:2.26) when Mn<sup>4+</sup> is used out. The optimum molar ratio of Mn:P is 1:4 (with Mn<sup>4+</sup>) and is 1:2 (with Mn<sup>2+</sup>). All other reaction parameters are as described for the zinc fertilizer. The manganese salt (preferably manganese dioxide), is mixed with phosphoric acid and heated at 150°C or above, under vacuum or under normal atmospheric pressures until at least a thick viscous material is formed. This may contain a small amount of unreacted particles. At this stage, manganese dihydrogen phosphate is formed. Further heating of this compound at temperatures above 200°C produces manganese polyphosphates. Optimally, the reaction is carried out at 300°C. Polymerisation is allowed to proceed till the compound retains its solubility in the testing reagents. Manganese polyphosphates have high water

solubility. To reduce water solubility and improve physical characteristics of the product, manganese polyphosphate is further neutralised with a basic compound such as lime, ammonia, magnesium oxide, etc. to a pH between 5 and 6. Best results are obtained with magnesium oxide and a neutralisation pH of 5.3. Following neutralisation, the product is dried and sieved. Apart from iron, which is a micronutrient, the fertilizer also contains nitrogen or magnesium, both of which are also micronutrients and add to the value of the fertilizer.

(v) Cobalt fertilizers

Starting materials include cobaltous oxide, sulphate or <sup>2+</sup>chloride which may contain upto 78.6%, 38.0% and 45.3% Co respectively. The cobalt raw material is added to phosphoric such that the molar ratios of Co:P is at least 1:2 (weight ratio Co:P = 1:1.05). The optimum molar ratio of Co:P is 1:2. All other reaction parameters are as described for zinc fertilizers.

(vi) In an embodiment of this invention, additives such as alkali or alkaline earth metal compounds are used for improving the solubility of the micronutrient polyphosphates in acids and complexants.

Additives are useful in improving the solubility

characteristics of a polyphosphate, particularly those of the trivalent and tetravalent metals. Thus  $\text{Fe}^{3+}$  polyphosphates rapidly form highly insoluble polyphosphates and arresting the reaction at the desired stage may be difficult. In such cases the use of additives is advocated.

Starting materials are any of the materials described earlier. To these, magnesium oxide or carbonate, potassium hydroxide or carbonate or sodium hydroxide or carbonate is added such that the molar ratio of the metal ion, M : additive is at any level from 1:0 or higher. The micronutrient compound and the additive are added to phosphoric acid whose proportion is in excess of that described in sections (i) to (v). This excess amount is in order to compensate for the additive. Thus, optimally, for each mole of divalent cation additive, 2 moles of P is added in excess as phosphoric acid; similarly for each mole of monovalent cation as additive 1 mole of P is added in excess. The reaction is carried out as described earlier for zinc fertilizers.

(vii) In a further embodiment of this invention fertilizers are prepared containing multiple micronutrient formulations.

Two or more types of micronutrient starting materials



are taken in any desired proportion. Additives are also added as described in section (vi). These are added to phosphoric acid which is taken in a proportion as mentioned in sections (i) to (vii). The reaction is then carried out as described in section (i).

The principle underlying the production of slow-release micronutrient fertilizers according to the process of the present invention, is that when metals and their oxides, hydroxides or carbonates are heated with phosphoric acid, and water is removed from the reacting mixture, the dihydrogen orthophosphates are produced. When sulphates or chlorides of the metal ions are used for reaction, heating results in loss of water and some sulphuric or hydrochloric acid leaving a residue of mixed sulphates/chlorides and orthophosphates. On further heating the polyphosphates, linear polyphosphate chains are formed which have  $-P-O-P-O-P$  linkages. The negatively charged O atoms on the  $P-O-P$  chains are the sites to which micronutrient cations like  $Zn^{2+}$ ,  $Cu^{2+}$ ,  $Fe^{3+}$ , etc. or  $H^+$  ion is attached. The cations with double or triple charges may also cross-link adjacent  $P-O-P$  chains to form a 3-D structure which may have low solubility in acids and complexants. For this reason additives like  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$  etc. help in reducing the number and bond strength of such cross-linkages of  $P-O-P$  chains and thereby improving solubility characteristics. Polymerisation is not allowed to proceed up to

the stage where very long chain metaphosphates are formed since such compounds are highly insoluble and the micronutrients in them are not available to plants. Polymerisation is stopped when the polyphosphates are not fully polymerised and the products show good solubility in dilute acids and complexants. Polyphosphates with these solubility parameters contain nutrients in a form that is available for plant uptake. However, such polyphosphate which are of incompletely polymerised are hygroscopic and acidic. Both these undesirable characteristics are due to the presence of hydrogen ions on the partially polymerised polyphosphate chain. Neutralisation of such acid groups with bases, renders the product non-hygroscopic as well as non-acidic. It also reduces the water solubility of the polyphosphate.

This invention presents a substantial improvement over previous processes for the production of slow-release micronutrient fertilizers. In this process, the initial reaction between metal compounds and phosphoric acid is carried out at temperatures above 150°C to speed up the reaction and remove moisture. Since 150°C is close to the boiling point of phosphoric acid evaporation is very slow and, therefore, for purposes of commercial production temperatures above 150°C are more appropriate since the process is significantly faster. This invention :

includes the new concept that, the extent to which any micronutrient phosphate should be polymerised is limited by the solubility of the polyphosphate product in dilute acids and solutions of complexants. Thus any suitable temperature above 150 °C may be chosen for producing the polyphosphate and the reaction is stopped at any stage before insolubilisation in the aforesaid reagents.

Accordingly, this invention provides a process for the production of slow-release fertilizers of all cationic micronutrients, in single- or multinutrient forms. The products have low water solubility but the nutrients are in a form available to plants. The fertilizers are also non-toxic, non-hygroscopic, easy to apply and exhibit improved fertilizer-use efficiency.

The main advantage of this process is the significant reduction in production time for the initial reaction stage between phosphoric acid and micronutrient compounds. Another advantage of this process is the simple technique of assessing the upper limit of polymerisation whereby the process is rendered extremely flexible as regards choice of temperature for polymerisation and components in reacting mixture. Thus, a wide range of starting materials may be used in widely ranging proportions and the polymerisation can be carried out at any

convenient temperature; the polymerisation is stopped once a simple test reveals that the upper limit of polymerisation is reached. Lastly, the process on the whole is simple, requires lower energy inputs than all previous processes and is readily adaptable to a wide range of micronutrient formulations.

The invention will now be explained in greater detail with the help of the following non-limiting examples.

Examples for zinc fertilizer

Example 1

Phosphoric acid (containing 52%  $P_2O_5$ ) was taken in a stainless steel tray. To 160 g of the acid 50 g of zinc ash (containing 72.1% Zn) was added. The material was allowed to stand for 30 min for frothing to subside. Frothing is due to the reaction of metallic zinc with acid. The mixture was then put into a muffle furnace at 170°C and heated until a mostly dried product was formed which is mostly  $Zn(H_2PO_4)_2$ . The temperature of the furnace was increased to 350°C and the material was further heated for 60 min. Preliminary trials had shown that heating beyond this period to 70 min and more results in the formation of polyphosphates which are not completely soluble in 0.1N HCl, 0.33M citric acid and 0.005 M DTPA. The solubility of the polyphosphate was tested in these reagents; 0.5g of the polyphosphate dissolved in 150 ml 0.1N HCl, 40 ml 0.33 M citric acid and 350 ml 0.005 M DTPA within 15 min. The average chain length (n) of the polyphosphate was 2.5.

The polyphosphate was allowed to cool to ambient temperature it was made into a paste with water and 58.5 ml of 25%  $\text{NH}_3$  solution was added to it. The pH after neutralisation was 4.0. The slurry was stirred and dried in an oven at 80°C. The dried material was ground in a mortar and sieved through 100 mesh B. S.

The material thus obtained had the composition 21% Zn, 19.1% P and 5.1% N. In 0.1 N HCl, 0.33 M citric acid and 0.005 M DTPA, the Zn in it is almost 100% soluble. About 7.5% of the Zn in it was soluble in water. The fertilizer remained undissolved in water for several months. Field trials with the fertilizer showed that 1.14 kg Zn added as this slow-release fertilizer increased the yield of paddy by 400-600 kg/ha in the first crop and to a similar extent in the second crop (residual effect). The requirements of this zinc fertilizer are about one-fifth to two-fifth the normal recommended dose for zinc sulphate. This fertilizer is also very effective in soils where zinc sulphate shows little response.

#### Example II

The entire process was the same as in example 1 except that during neutralisation 82 g  $\text{CaCO}_3$  was used instead of ammonia. The composition of this sample was 19.5% Zn, 18% P and 9.6% Ca.

### Example III

The entire process was the same as in Example I except that during neutralisation 46 g KOH dissolved in about 80 ml water was used instead of ammonia solution.

### Example IV

The entire process was the same as in Example I except that zinc oxide (containing 78% Zn) was used instead of zinc ash, as the starting material. 100 g of the zinc oxide was reacted with 324 g phosphoric acid containing 52%  $P_2O_5$ . The composition of the fertilizer obtained was as follows 22.9% Zn, 25.0% P and 4.7% N.

### Example V

The entire process was the same as Example I except that metallic zinc (zinc dust containing about 98% Zn) was used instead of zinc ash, as the starting material. 100 g of zinc dust was reacted with 409 g of phosphoric acid containing 52%  $P_2O_5$ .

### Example VI

Phosphoric acid containing 23%  $P_2O_5$  was taken in a stainless steel tray. To 370 g of the acid 50 g of zinc ash (containing 72.1% Zn) was added. It was allowed to stand for about 30 min for the frothing to subside. This was subsequently put into a muffle furnace and heated at 200°C till the product was almost dry. The furnace temperature was then increased to 300°C and the sample heated for 90 min. solubility of the

polyphosphate in 0.1 N HCl, 0.33 M citric acid and 0.005 M DTPA was tested. The polyphosphate dissolved in these reagents within 15 min. After cooling to ambient temperature it was made into a paste with about 30 ml water and 58.5 ml of 25% ammonia solution was added to it. The pH after neutralisation was 4.0. The material was dried in an oven at 60°C ground and sieved through 100 mesh B.S. The material thus obtained had the composition 20.9% Zn, 18.9% P and 5.5% N. Other characteristics were similar to the fertilizer described in Example 1.

Example for copper fertilizer

Example VII

10 g cupric hydroxide (containing 53.6% Cu) was taken in a porcelain dish. To this 38 g phosphoric acid [containing 46.4%  $P_2O_5$  (w/w)] was added. The molar ratio of Cu:P was, thus, 1:3. The mixture was placed in a muffle furnace at 180°C till a clear viscous material was obtained. This was further heated at 250°C for 60 min. The cupric polyphosphate was tested for its solubility. It was observed to be soluble in 0.1N HCl, 0.33 M citric acid and 0.005 M DTPA within 30 min. The sample was made into a slurry with a few ml water and neutralised to pH 4.0 with 10% NH<sub>3</sub> solution (about 8 ml). It was then dried in an oven at 80°C, ground and sieved through 100 mesh B.S.

The fertilizer had the composition 13.6% Cu, 19.6% P

and 16.3% N. It had an average chain length (n) of 2.65 and 5.2% of total Cu was soluble in water.

The material remained stable in contact with water for several months. It was completely soluble in the dilute acids and complexants mentioned above. Plant growth trials with paddy showed significant increase in yields over the control at dosages as low as 2.0 kg/ha Cu; at this level copper sulphate does not result in any yield increase.

#### Example VIII

10 g cupric chloride (containing 36.5% Cu) was taken in a porcelain crucible. Phosphoric acid (containing 50% P<sub>2</sub>O<sub>5</sub>) was added such that the molar ratio Cu:P was 1:3 (24.5 g acid added). The crucible was put into a muffle furnace at 170°C and heated till a dried substance, was obtained having a light green colour. This was again heated at 200°C for 30 min. During this period samples of the polyphosphate were periodically taken and tested for their solubility in 0.1 N HCl, 0.33 M citric acid and 0.005 M DTPA. The sample was removed from the furnace at that stage when the material begins to solubilise slowly (within 30 min) but insoluble materials are not yet formed. The average chain-length (n) of the polyphosphate was 2.5.

The polyphosphate was cooled to room temperature, made



into a slurry with a few drops of water and then neutralised with 10% ammonia solution upto a pH of 4.0. This was dried in an oven at 70 C, powdered and sieved through 150 mesh B.S.

#### Example IX

To 10 g cupric carbonate (containing 50.0% Cu) 24 g of phosphoric acid (46.4% P<sub>2</sub>O<sub>5</sub>) was added so that the molar ratio of

Cu:P = 1:2. This was placed in a muffle furnace at 180 C and heated till almost dry. This was further heated at 225 C for 45 min. The remaining procedure is the same as that described in Example VII.

Samples for iron fertilizer

#### Example X

The starting material was synthetic goethite [ $\alpha$ -FeO(OH)] containing 60%. To 1750 g of phosphoric acid (containing 39.7% w/w of P<sub>2</sub>O<sub>5</sub>), 100g goethite and 130g magnesium oxide were added and the mixture was stirred. The amount of phosphoric acid taken was such that the Fe:P molar ratio was 1:3 plus an excess amount such that the Mg:P molar ratio was 1:2. This was placed in a muffle furnace in flat trays (ss 316L) and heated at 180 C till it was almost dry. The temperature of the furnace was subsequently increased to 250 C and the sample was heated for 10 min. Solubility of the sample was tested at periodic intervals, in 0.1N HCl, 0.33 M citric acid, and 0.005 M DTPA. Solubility of the polyphosphates in these reagents increases with period of

heating, reaches a maximum and declines again. The ideal polyphosphate would be around the region of the maximum. Water solubility of the polyphosphate and the material after neutralisation were also tested; polyphosphates having lowest water solubility are preferred. Thus, although the polyphosphate obtained after heating at 250°C for 10 min and 20 min have similar solubilities in acids and complexants, the neutralised products of the former has much lower water solubility than that of the latter. Therefore the material obtained at 250°C after 10 min heating was preferred. The weight loss of the polyphosphate at this stage is about 9g/100g  $\text{H}_3\text{PO}_4$  in the reaction mixture. This corresponds to 53% polymerisation.

The polyphosphate is cooled to ambient temperature, made into a paste with water and neutralised with dilute ammonia solution (containing about 12.5%  $\text{NH}_3$ ) till the pH of the slurry was around 5.4. This required 1.75l of 12.5% ammonia solution. The slurry was stirred and dried in an oven at 70°C, it was hand ground and sieved through 80 mesh BS. The fertilizer was completely soluble in 0.1N HCl, and 0.33M citric acid but only 5% was soluble in water.

#### Example XI

The entire process was the same as in Example X except that magnesium oxide was used for neutralisation instead of

ammonia solution. In this case the pH of the solution was raised to 4.5 by addition of MgO (about 550 g). The suspension was heated to 60 C and stirred for one hour. It was subsequently processed as described earlier.

The product contained 3.7% Fe, 45.4%  $P_2O_5$  and 25.3% Mg. It had a water solubility of around 0.1%. Other parameters were the same as for Example X.

#### Example XII

The process is essentially the same as in Example X and XI except that natural goethite (containing 45% Fe) is used instead of synthetic goethite. 100g natural goethite, 95g magnesium oxide and 1520g phosphoric acid (containing 39.7%  $P_2O_5$ ) were mixed and processed as described in Example X. Polymerisation, in this case, was carried out at 200 C for 25 min till a weight loss of about 7g/100g  $H_3PO_4$  in the reaction mixture, was obtained. The polyphosphate was neutralised with ammonia solution (12.5%, 1.65 l) to a pH of around 5.4 and subsequently processed as in Example X. The properties of the two materials were similar.

#### Example XIII

100g manganese dioxide (pyrolusite) containing 63.4% Mn was mixed with 580g of phosphoric acid containing 51%  $P_2O_5$  (Mn:P ratio in the mixture = 1:4). This was taken in a porcelain

crucible and heated at  $170^{\circ}\text{C}$  till a thick gel-like material was formed. The temperature of the furnace was raised to  $300^{\circ}\text{C}$  and the crucible was kept in it for 50 min. Thereupon a dark purple, hard solid was formed, which had the maximum solubility in the testing reagents. The corresponding weight loss was  $15.4\text{g}/100\text{g}$   $\text{H}_3\text{PO}_3$  in the reaction mixture, which produces about 55% polymerisation.

The polyphosphate was cooled to ambient temperature, made into a paste with water and neutralised with magnesium oxide to a pH of about 5.3. About 400 g  $\text{MgO}$  was required; after addition the slurry was stirred at  $60^{\circ}\text{C}$  for about one hour for completion of the reaction. The material was dried at  $70^{\circ}\text{C}$ , ground and sieved through 100 mesh BS. The fertilizer contained 7.5% Mn, 35.3%  $\text{P}_2\text{O}_5$  and 29% Mg. Solubility in water was about 0.1% but in 0.1 N  $\text{HCl}$  and 0.33M citric acid it was soluble to the extent of about 90-95%.

#### Example XIV

10g cobalt oxide was mixed with 51g phosphoric acid of 50% strength to give a Co:P ratio of 1:3. To this 67.7g potassium hydroxide and a further 170g phosphoric acid were added to give K:Co=10:1 and K:P=1:1. The slurry was heated at  $180^{\circ}\text{C}$  till dried. This was further heated at  $250^{\circ}\text{C}$  for 30 min to obtain the mixed

polyphosphate of potassium and cobalt. The polyphosphate was cooled to ambient temperature, made to a paste with water and neutralised with potassium hydroxide to pH 5. Subsequently it was ground with a hand mortar and sieved through 100 mesh. The fertilizer was completely soluble in 0.1N HCl and 0.33 M citric acid.

#### Example XV

100g natural goethite and 100g manganese dioxide were mixed with 1.541 phosphoric acid (containing 40%  $P_2O_5$ ). The mixture was put into a muffle furnace and heated at 200°C for 50 min whereupon a mostly homogenous gel was obtained. The temperature of the furnace was raised to 350°C and the sample was heated for 30 min. Optimum polymerisation was tested as described in the previous Examples. Subsequent processing was done as described in Example XIII except that 900 g of magnesium oxide was required for neutralisation of the polyphosphate. This fertilizer containing both iron and manganese, has low water solubility (about 2%) but high solubility in dilute acids and complexants.

WE CLAIM

1. A process for preparation of slow release cationic micronutrient fertilizers, which processes comprises heating at least one micronutrient metal or a compound thereof <sup>such as herein described</sup> with or without additives <sup>such as herein described</sup> with phosphoric acid till the resultant mixture is mostly homogenous, further heating to form <sup>the corresponding</sup> metal polyphosphates of such a degree of polymerisation that they are still soluble in dilute mineral acids and complexants, treating said metal polyphosphates with a basic compound and finally obtaining a dried powder.
2. A process as claimed in claim 1, wherein the phosphoric acid used has a concentration upto 60% P<sub>2</sub>O<sub>5</sub> by weight.
3. The process as claimed in claim 1, wherein the phosphoric acid used has a concentration of 30 to 60% P<sub>2</sub>O<sub>5</sub> by weight.
4. The process as claimed in claim 1, wherein, said micronutrient metal is selected from zinc, copper, iron, maganese, cobalt.
5. The process as claimed in claim 1, wherein the micronutrient metal of the oxide, hydroxide, chloride or sulphate the of micronutrient metal is used for the reaction with phosphoric acid.

6. The process as claimed in claim 1, wherein various additives such as the oxides, hydroxides, or carbonates of magnesium, calcium, potassium or sodium may also be added to the reaction mixture before heating with phosphoric acid.

7. The process as claimed in claim 1, wherein the ratio of metal cation:additive cation is atleast 1:8.

8. The process as claimed in claim 1, wherein the molar ratio of metal cation:additive cation is in the range 1:2 to 1:10.

9. The process as claimed in claim 1, wherein the amount of phosphoric acid used for the first step of heating with the micronutrient metal or a compound thereof, is sufficient to produce the dihydrogen phosphates of the cations present.

10. The process as claimed in claim 1, wherein for every mole of metal ion,  $M^{n+}$ , in the reaction mixture, the molar proportion of phosphoric acid is at least  $n$  times that of the metal, where  $n$  denotes the valance of the metal ion.

11. A process as claimed in claim 1, wherein during the first step of heating with phosphoric acid for every mole of divalent cation present, phosphoric acid containing at least 2 moles  $P$  is added for every mole of trivalent cation present, phosphoric acid containing at least 3 moles  $P$  is added, and for

every mole of tetravalent cation present, phosphoric acid containing at least 4 moles P is added.

12. A process as claimed in claim 1, wherein during the first step of heating with phosphoric acid, if an additive is used then an additional amount of phosphoric acid is added in quantities such that  $M^{n+} : P$  is at least 1:n or more, where n is the valance of the additive cation,  $M^{n+}$ .
13. A process as claimed in claim 1, wherein the first step of heating with phosphoric acid is carried out at any temperature above 150° C under mostly ambient pressure.
14. A process as claimed in claim 1, wherein the first step of heating with phosphoric acid is carried out at any temperature above or below 150° C under vacuum.
15. A process as claimed in claim 1, wherein step of further heating to form the metal polyphosphates is carried out at temperatures above 200° C.
16. A process as claimed in claim 15, wherein, the step of further heating to form the metal polyphosphate is carried out at a temperature in the range of 250° and 350° C.
17. A process as claimed in claim 1, wherein the step of



further heating to form the metal polyphosphate is carried out till polymerisation occurs and the compound shows reduced solubility in water.

18. A process as claimed in claim 1, wherein the step of further heating to form the metal polyphosphates is carried out till the product shows high solubility in dilute acids and complexants.

19. A process as claimed in claim 1, wherein the step of further heating to form the metal polyphosphates is carried out upto the point where the upper limit of its solubility, in dilute acids and complexants is reached.

20. A process as claimed in claim 1, wherein the solubility of the metal polyphosphate is tested using 0.1 N hydrochloric acid, 0.33 M citric acid and/or 0.005 M DTPA (diethylene triamine pentaacetic acid).

21. A process as claimed in claim 1, wherein for the step of neutralisation, a basic compound such as ammonia, lime, magnesium oxide, potassium hydroxide is used.

22. A process as claimed in claim 1, wherein the neutralisation is carried out after addition of water to form a paste or slurry.

23. A process as claimed in claim 1, wherein for the step of neutralisation the pH of the slurry is above 4.

24. A process as claimed in claim 1, wherein the pH of neutralisation is between 4.5 and 5.5.

25. A process as claimed in claim 1, wherein for the step of neutralisation using water-insoluble bases such as magnesium oxide or lime, the reaction mixture is stirred and warmed.

26. A process as claimed in claim 25, wherein the reaction mixture is warmed to 60 C.

27. A process as claimed in claim 1, wherein the product from the step of neutralisation is dried till it is essentially free of moisture.

28. A process as claimed in claim 1, wherein the product from the step of neutralisation is dried at temperatures below 100 C.

29. A process as claimed in claim 1, wherein the dried product is ground to a powder.

30. A process as claimed in claim 1, wherein the product is ground to pass through a 100 mesh BS sieve.

31. A process for the manufacture of slow-release micronutrient fertilizers substantially as herein described and as illustrated in the examples(s).

Dated this 10th day of APRIL 2000.

*S. S. DAVAR*  
(S. S. DAVAR)  
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APPLICANTS' AGENT

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